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CARBORANE BURNING RATE MODIFIERS.(U)  
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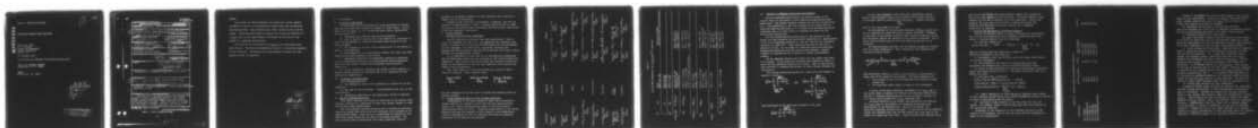
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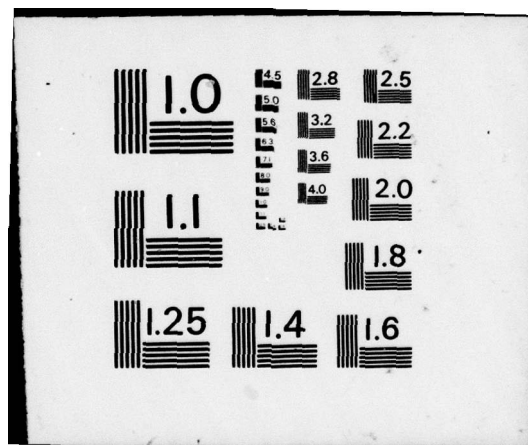
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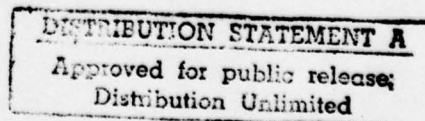
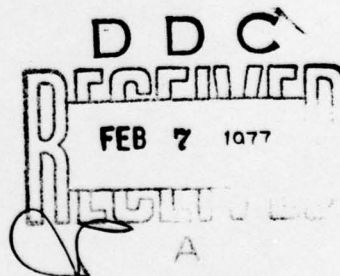
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Figure 6. Report Documentation Page.

## Summary

Derivatives of ortho-carborane with functional groups capable of adding to the C=C in polybutadiene binders have been synthesized and characterized. Most promising are those containing Si-H and SH groups. These have been shown to bond to the binder and addition of a  $B_{10}C_2$  cage to the binder seems to increase the affinity of the binder for carborane plasticizers.

The kinetics of the reaction of  $B_{10}H_{12}L_2$  with acetylenes have been studied. The reaction proceeds by loss of L followed by formation of the carborane. Acetylenes with electronegative groups give the highest yields of carborane.

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## A. Introduction

### I. Carborane - Advantages

The advantages and disadvantages of using carboranes as burning rate promoters have been examined in detail in recent years. Earlier reports by W.E. Hill, et. al, at Rohm and Haas clearly demonstrated the following:<sup>1,2,3</sup>

(1) Carboranes are effective burning rate promoters.

(2) Loss of specific impulse due to the addition of carboranes is not a serious problem in composite and double base systems of high solids loading.

(3) The increase in burning rate is proportional to the amount of boron in the propellant.

(4) There appear to be no synergistic effects with boron and other known burning rate promoters such as iron.

(5) Mechanical properties of propellants containing carboranes are not completely satisfactory but polybutadiene-based propellants with very high solids loadings have reasonable good mechanical properties.

(6) Of all carboranes scanned by the author of these reports, n-hexylcarborane was the most desirable due to its compatibility and plasticizer capabilities.

### II. Carborane - Disadvantages

Chief disadvantages are:

(1) The tendency of many of the carboranes to migrate out of the propellant.

(2) The cost of the carboranes. N-hexylcarborane may cost as much as \$2,000/lb.

(3) Mechanical properties of the propellants should be improved.

### B. Specific Program Objectives

This report contains the results of work done by the authors under contract with the U.S. Department of Navy, Sea Systems Command in order to eliminate these disadvantages.

The first specific program objective was to synthesize carboranes containing groups that would allow the carborane to be attached to the polybutadiene binder. This was to be accomplished by addition of the functional group across the C=C bond in the binder backbone. The next objective was to demonstrate that these carboranes could be

attached to the binder backbone and thus eliminate their ability to migrate out of the propellant.

Because of the high cost of decaborane ( $\sim \$900/\text{lb.}$ ) and the low yields of n-hexylcarborane ( $\sim 30\%$ ), a further objective was to study the kinetics of carborane and to determine the best routes (high yield) to desired carboranyl derivatives.

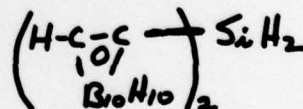
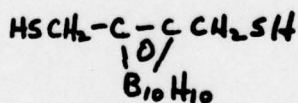
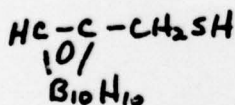
### C. Program Results

#### I. Synthesis of Functional Carboranes.

Several functional carboranes have been synthesized. Table I lists the compounds and their m.p. and summarizes the synthetic path. Table II contains the distinctive IR and NMR absorptions and assignments for the compounds. For convenience, the parent carborane was prepared and the derivatives synthesized by reaction with butyl lithium followed by the appropriate reagent.

It is significant to note that all of the additives synthesized and evaluated were solids with the exception of the silicon-containing carboranes. Both of these derivatives were low viscosity liquids and hence are more desirable as burning rate additives since high solids loadings would be possible.

Very small amounts of three derivatives not listed in Table I were also prepared. These compounds were:



All were obtained in very low yield as solids and therefore were not further studied.

#### II. Isomerization Studies of Ortho to Meta Carboranes

Isomerization of the ortho analogs to their meta counterparts usually results in a change of  $\sim 30^\circ\text{C}$  with the meta analog melting lowest (i.e. ortho-n-hexylcarborane melts at  $+5^\circ\text{C}$  while meta-n-hexylcarborane melts at  $-27^\circ\text{C}$ ). Therefore isomerization of the solids reported here was not expected to give liquids at room temperature. Clearly a depression of  $\sim 30^\circ\text{C}$  is important only when the physical properties of the additive are marginal.

Table 1

Carborane	m.p., °C	Route
$\text{H}-\text{C}-\text{C}-\text{SH}$ $\text{B}_{10}\text{H}_{10}$	230-235°C	$\text{HC}-\text{C}-\text{C}-\text{Li} + \text{S} \xrightarrow{\text{H}^+} \text{H}-\text{C}-\text{C}-\text{SH}$ $\text{B}_{10}\text{H}_{10}$
$\text{HS}-\text{C}-\text{C}-\text{SH}$ $\text{B}_{10}\text{H}_{10}$	300-302°C	$\text{Li}-\text{C}-\text{C}-\text{Li} + \text{S} \xrightarrow{\text{H}^+} \text{HS}-\text{C}-\text{C}-\text{SH}$ $\text{B}_{10}\text{H}_{10}$
$\text{CH}_3-\text{C}-\text{C}-\text{Si}(\text{CH}_3)_2\text{H}$ $\text{B}_{10}\text{H}_{10}$	-18°C	$\text{CH}_3-\text{C}-\text{C}-\text{Li} + \text{Cl}-\text{Si}(\text{CH}_3)_2\text{H} \rightarrow \text{CH}_3-\text{C}-\text{C}-\text{Si}(\text{CH}_3)_2$ $\text{B}_{10}\text{H}_{10}$
$\text{H}(\text{CH}_3)_2\text{Si}-\text{C}-\text{C}-\text{Si}(\text{CH}_3)_2\text{H}$ $\text{B}_{10}\text{H}_{10}$	-10°C	$\text{Li}-\text{C}-\text{C}-\text{Li} + 2\text{ClSi}(\text{CH}_3)_2\text{H} \rightarrow \text{H}(\text{CH}_3)_2\text{Si}-\text{C}-\text{C}-\text{Si}(\text{CH}_3)_2$ $\text{B}_{10}\text{H}_{10}$
$(\text{Me}_2\text{N})_2\text{P}-\text{C}-\text{C}-\text{P}(\text{NMe}_2)_2$ $\text{B}_{10}\text{H}_{10}$	114.5-117.5°C	$\text{Li}-\text{C}-\text{C}-\text{Li} + 2\text{Cl}-\text{P}(\text{NMe}_2)_2 \rightarrow (\text{Me}_2\text{N})_2\text{P}-\text{C}-\text{C}-\text{P}(\text{NMe}_2)_2$ $\text{B}_{10}\text{H}_{10}$
$\text{H}-\text{O}-\text{CH}_2-\text{C}-\text{C}-\text{CH}_2\text{OH}$ $\text{B}_{10}\text{H}_{10}$	298-300°C	$\text{CH}_3\text{COCH}_2\text{C}-\text{C}-\text{CH}_2\text{OCH}_3 \xrightarrow[\text{NaOH}]{\text{H}^+} \text{HOCH}_2\text{C}-\text{C}-\text{CH}_2\text{OH}$ $\text{B}_{10}\text{H}_{10}$
$\text{Hg}-\left(\text{C}-\text{C}-\text{CH}_3\right)_2$ $\text{B}_{10}\text{H}_{10}$	172°C decomp.	$\text{CH}_3-\text{C}-\text{C}-\text{Li} + \text{HgCl}_2 \rightarrow \text{Hg}\left(\text{C}-\text{C}-\text{CH}_3\right)_2$ $\text{B}_{10}\text{H}_{10}$
$(\text{Me}_2\text{N})_2\text{P}-\text{C}-\text{C}-\text{P}\emptyset_2$ $\text{B}_{10}\text{H}_{10}$	138-140°C	$\emptyset\text{P}-\text{C}-\text{C}-\text{Li} + \text{ClP}(\text{NMe}_2)_2 \rightarrow \emptyset_2\text{PC}-\text{C}-\text{P}(\text{NMe}_2)_2$ $\text{B}_{10}\text{H}_{10}$



Table 2

IR and NMR Parameters for  $B_{10}H_{10}C_2R^1R^2$  Compounds

$R^1$	$R^2$	$^1H_{NMR}$ $\delta$ ppm from TMS	Selected Infrared Absorptions $cm^{-1}$ and Assignments
H	SH	$\delta SH = 3.85$ ppm $\delta CH = 3.45$ ppm	
SH	SH	$\delta SH = 3.73$ ppm	
$H(CH_3)_2Si$	$Si(CH_3)_2H$	$\delta CH_3-Si = 0.36$ ppm $\delta Si-H = 4.22$ ppm $JH-CH_3 = 4Hz$	$\nu B-H = 2591$ $cm^{-1}$ $\nu Si-H = 2169$ $cm^{-1}$ $\delta cage = 725$ $cm^{-1}$
$CH_3$	$Si(CH_3)_2H$	$\delta CH_3-C = 1.98$ ppm $\delta CH_3-Si = 0.36$ ppm $\delta Si-H = 4.23$ ppm $JH-CH_3 = 4.8Hz$	$\nu B-H = 2595$ $cm^{-1}$ $\nu Si-H = 2164$ $cm^{-1}$ $\delta cage = 722$ $cm^{-1}$
$P(NMe_2)_2$	$P(NMe_2)_2$	$\delta CH_3 = 2.8$ ppm $Jp-CH_3 = 5.2Hz$	
$P\phi_2$	$P(NMe)_2$	$\delta CH_3-N = 2.79$ ppm $\delta \phi = 7.50$ ppm $Jp-CH_3 = 9.0$ Hz	$\nu B-H = 2597$ $cm^{-1}$ $\nu P(NMe_2)_2 = 971$ $cm^{-1}$ $\delta cage = 722$ $cm^{-1}$
$HOCH_2$	$CH_2OH$	$\delta CH_2 = 4.3$ ppm	$\nu OH = 3333$ $cm^{-1}$ $\nu BH = 2597$ $cm^{-1}$ $\delta cage = 719$ $cm^{-1}$
$CH_3$	$Hg-C-C-CH_3$ $\diagup$ $B_{10}H_{10}$	$\delta CH_3-C = 1.90$ ppm	$\nu BH = 2597$ $cm^{-1}$ $\delta cage = 719$ $cm^{-1}$

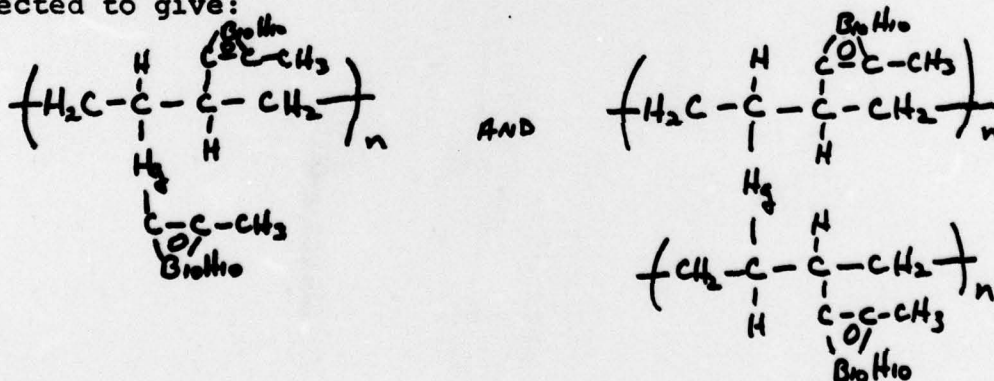
### III. Additions to Hydroxy-terminated Polybutadiene.

Hydroxy-terminated polybutadiene was chosen because of its current choice as the binder in most composite polybutadiene-based propellants. The polymer backbone contains one C=C per 54 mass units [i.e.  $(-\text{H}_2\text{C}-\text{CH}=\text{CH}-\text{CH}_2-)_n$ ] and thus mixtures of the binder and the carborane additive were made in a 1:1 molar ratio for mono-functional carboranes and a 1:2 molar ratio of carborane to binder for the difunctional derivatives.

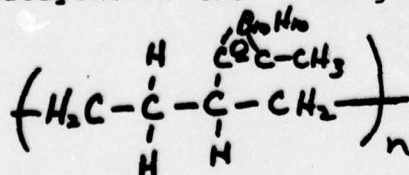
For the silicon-containing derivatives, the reaction of the binder with the carborane was monitored by observing the disappearance of the Si-H stretching vibration at  $260\text{ cm}^{-1}$  and the C=C stretching vibration at  $\sim 1640\text{ cm}^{-1}$ . These reactions were run at  $90^\circ\text{C}$  for a period of 24 hrs. In all cases the vibrations which were monitored disappeared, indicating that the reaction was complete. Further evidence of reaction was the formation of elastic polybutadiene rubbers.

The SH compounds reacted much faster with the binder than their Si-H analogs. In all cases the reactions were complete in about 12 hours and the resulting polymers were solids. Some of these solids were difficult to characterize because of their extreme hardness and insolubility.

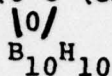
Bis(1-methyl-carboranyl)mercury(II) reacts with the polymer as expected to give:



Acid hydrolysis of the above gave polymers of the type



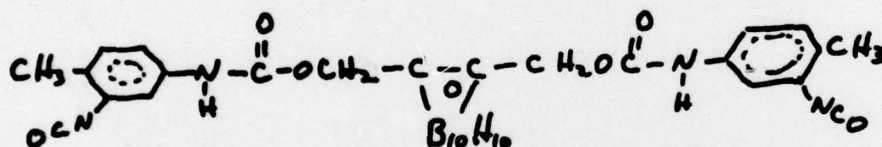
We feel that polymers of this type show considerable promise since n-hexylcarborane could even be fixed to this binder system by an analogous reaction using  $\text{Hg}-(\text{C}-\text{C}-(\text{CH}_2)_5\text{CH}_3)_2$ . However much more



work in this area needs to be done.

The derivatives of the carboranes containing  $\text{P}(\text{NMe}_2)_2$  groups were not as compatible as those derivatives already mentioned. Attempts to add these to the polymer backbones under similar conditions failed and frequently gassing was observed as the reaction proceeded. Due to these results further work we feel with these derivatives is not warranted.

Bis(hydroxymethyl)carborane can be prepared in situ and reacted with the binder immediately. Thus, reaction of the carborane with toluenediisocyanate gives:



This derivative, which is a solid, can be used as a curing agent to react with the OH groups of the polymer. The chief drawbacks are:

1. The presence of only two OH groups per high molecular weight polymer and
2. The relatively small amount of boron in the diisocyanate.

In spite of the above drawbacks, attachment of a  $\text{B}_{10}\text{C}_2$  cage to the binder seems to improve the affinity for carborane plasticizers and thus a carborane plasticizer may not be as prone to migrate out of a binder cross-linked with a  $\text{B}_{10}\text{C}_2$  carborane cage.

Increased affinity of the binder once modified by the addition of a  $\text{B}_{10}\text{C}_2$  cage to the backbone for carborane plasticizers was demonstrated in the following way. Mixes of the binder, the functional carborane and NHC were made. In the case of the SH compounds, solids were obtained even when the NHC content was twice that of the binder on a weight per cent basis. Similar results were obtained using

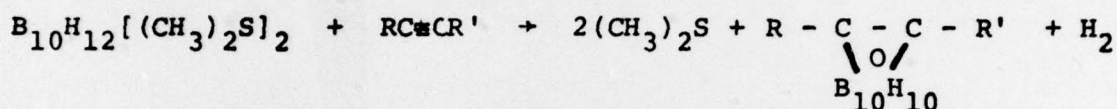


the silicon derivatives only polybutadiene rubbers were obtained in the latter case instead of solid materials. All mixes showed no great tendency for the NHC to migrate out of the propellant. Clearly the presence the  $B_{10}C_2$  cage on the binder is making the binder more carborane-like and hence the binder affinity for a carborane plasticizer is enhanced.

### C. Kinetics and Mechanism of Carborane Formation

Because of the small amount of  $B_{10}H_{14}$  available and the generally low yield of ortho-carboranes from acetylenes containing alkyl side chains, a detailed kinetic study was undertaken.

The reaction studied was:



Important kinetic data are summarized in Table III.

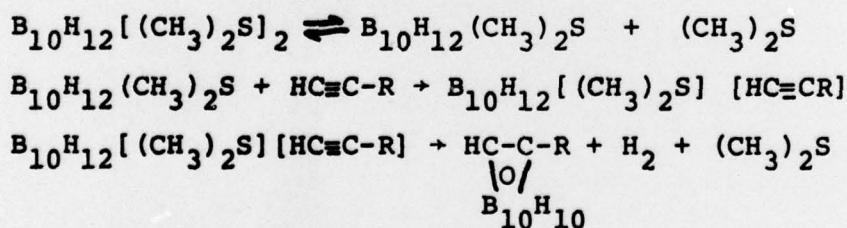
Conclusions reached in this study are:

(1) Acetylenes of the type  $HC\equiv CCH_2X$  give much higher yields when X is electron withdrawing.

(2) Side products in the reaction of  $B_{10}H_{12}[(CH_3)_2S]_2$  with acetylenes are hydroboration products with high molecular weight.

(3) Yields of ortho-carboranes are directly proportional to the Taft polar substituent constant  $\sigma^*$  for X. The higher the value of  $\sigma^*$ , the better the yield.

(4) Data best fits a mechanism:



(5) Steric factors do not seem especially important since yields of the carborane and  $\Delta S^\ddagger$  values using  $CH_3OC(O)CH_2C\equiv CCH_2C(O)OCH_3$  are similar to those of mono-substituted acetylenes.

(6) Functional groups adjacent to the  $C\equiv C$  group give very low yields. For example,  $HC\equiv C\phi$  or  $HC\equiv CCOC(O)CH_3$  gave only trace amounts of the appropriate carborane.

Subsequent to the submission of this proposal and prior to the funding of the proposal, some of the data given here was reported in a paper by the investigators.



Table III. Kinetic Data for Carborane Formation

Acetylenes	$\Delta H^\ddagger$ (kcal/mole)	$\Delta S^\ddagger$ (eu)	Rate Constant Sec <sup>-1</sup> , 37°C	Yields, %
HC $\equiv$ CCH <sub>2</sub> Br	36.1	40	$1.04 \times 10^{-4}$	90
HC $\equiv$ CCH <sub>2</sub> OC(O)CH <sub>3</sub>	34.9	34	$4.35 \times 10^{-5}$	85
HC $\equiv$ C(CH <sub>2</sub> ) <sub>3</sub> Cl	26.6	6	$1.80 \times 10^{-5}$	50
HC $\equiv$ C(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	26.4	6	$3.35 \times 10^{-5}$	30
HC $\equiv$ C(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	24.8	0	$2.62 \times 10^{-5}$	30
CH <sub>3</sub> C(O)OCH <sub>2</sub> CCH <sub>2</sub> OC(O)CH <sub>3</sub>	33.4	29	$5.2 \times 10^{-5}$	85

Attempts to use amines and ethers as Lewis bases in the  $B_{10}H_{12}L_2$  complexes were unsuccessful. Amines give  $B_{10}H_{10}^{-2}$  derivatives while ethers undergo complex reactions with  $B_{10}H_{14}$  to give alcohols and unidentified complex boron hydride products.

The importance and relevance of several other reaction conditions favorable to a high yield of carborane are somewhat obscure. The following discussion speculates about some of these factors:

- (1) Nonpolar solvents favor high yields.

The paper cited above suggests that the transition state leading to carborane is less polar than the side-reaction transition states. Saturated hydrocarbons or even perfluorocarbon solvents ought logically to be used, therefore, but have not been investigated carefully.

- (2) Polar solvents are undesirable. Polar solvents are generally basic in nature by virtue of an electronegative atom with at least one lone pair of electrons. It is known that "hard-base" atoms (oxygen and nitrogen) promote undesirable reactions like  $B_{10}H_{10}^{-2}$  formation by encouraging the acidic behavior of  $B_{10}H_{12}L_2$ . One may speculate that  $B_{10}H_{12}L$  - the putative species which reacts with acetylenes - is a stronger proton acid than  $B_{10}H_{12}L_2$ , since  $B_{10}H_{12}L$  is missing the electron pair of the lost ligand. Similarly,  $B_{10}H_{12}LA$  is expected to be a stronger proton acid than  $B_{10}H_{12}L_2$  because A is a weaker electron donor than L. It is possible that suppression of  $H^+$  ionization by deliberate addition of a very weak proton acid may reduce the loss of  $B_{10}H_{12}$  species to side reactions. The weak acid obviously should have a conjugate base of very low nucleophilicity.

- (3) Weakly polar solvents are also undesirable.

Attempts to reduce solvent polarity by changing from "hard-base" solvents (oxygen and nitrogen) to less electronegative heteroatoms were not successful. Sulfides and acetonitrile are poor reaction media in part because they severely reduce the concentration of active  $B_{10}H_{12}L$ . These solvents may also be expected to promote the acidic behavior of  $B_{10}H_{12}$  species, albeit less actively than the "hard-base" solvents. Paradoxically, some  $Et_2S$  (about 10%) in benzene appears to be beneficial, in spite of retardation of the rate of carborane formation. Perhaps the role of this added soft-base is to minimize exposure to  $B_{10}H_{12}L$  intermediate to minor impurities which are thermally destroyed in the early stages of the carborane formation process.

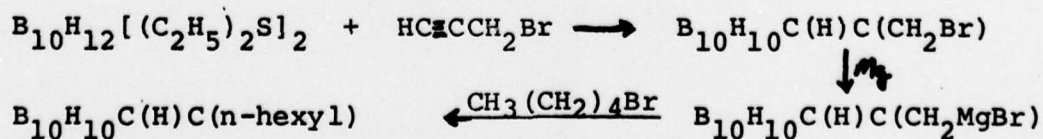
#### (4) Impurities lower yields

Impure  $B_{10}H_{12}L_2$  starting materials have a pronounced tendency to give lower yields than expected on the basis of pure  $B_{10}H_{12}L$  content. Usually this is attributed to separation problems of product and by-product, but the possibility exists that basic impurities (oxygen species or hydridic BH compounds) actually reduce the amount of carborane formed. Successive hydric hydrogens in one impurity molecule may serve to divert several  $B_{10}H_{12}L$  molecules from the desired carborane formation - the separation problem is then compounded by the presence of more by-product. Rigid purification of starting materials is known to be helpful, but the identity and role of the impurities is unfortunately obscure.

#### D. Conclusions

Several important conclusions have been drawn from this work. These are:

- (1) Carboranes containing Si-H, S-H, and Hg(-C-C-R) groups can be attached to the polymer backbone in polybutadiene  $B_{10}H_{10}$  binders.
- (2) Properties of the polymer resulting from the addition of the carborane to the binder vary with the type of carboranyl derivative used.
- (3) Isomerization from ortho-carboranes to meta-carboranes can help to lower the freezing point of the carboranyl additive but only by  $\sim 30^\circ C$ .
- (4) Of all the carboranes studied, the compounds containing silicon have the best physical properties.
- (5) Conversion of  $B_{10}H_{14}$  to ortho-carboranes is most efficient for highly electronegatively substituted acetylenes using current synthetic procedures. For example, the synthesis of n-hexylcarborane by the direct route involving  $B_{10}H_2[(C_2H_5)_2S]_2$  and octyne gives yields of  $\sim 30\%$ . A higher yield synthesis (but admittedly one that requires more steps) would be:





#### E. Suggestions for further study.

(1) Further synthesis of carborane additives which have the ability to bond to the polymer backbone should be carried out. Special emphasis should be placed on the ability of these additives to function as plasticizers themselves.

(2) The physical properties of the modified binders containing the carborane cage should be optimized.

(3) Propellant mixes should be made utilizing the additives. Burning rates and physical properties of the resulting propellants should be measured.

(4) Carborane synthesis using a range of solvents with different polarities should be studied.

(5) Base adducts of  $B_{10}H_{14}$  of the type  $B_{10}H_{12}L_2$  [L = very soft bases] need to be studied since there is some evidence that weaker bases may give better yields of carborane.

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